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A COMPUTER PROGRAM FOR GENERATING  
DEFORMATION MECHANISM MAPS FOR  
POLYMERS

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R.G. O'DONNELL

MRL-TN-592

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# A Computer Program for Generating Deformation Mechanism Maps for Polymers

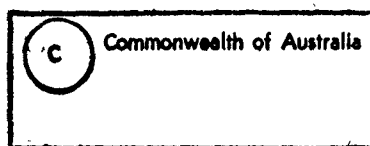
R.G. O'Donnell

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## Abstract

The deformation mechanism map is a means of representing the predominant mechanism of deformation within a material over a range of deformation conditions. This paper introduces a computer program which utilizes a number of theoretical models of deformation within amorphous polymers to identify "fields" within extension rate — temperature space where particular deformation mechanisms operate. The program is able to delineate these fields using borders and include isobars to indicate stress levels. Very good correlation is seen between the computer generated mechanism map and experimental results for PVC.

Whilst in its present form the program is restricted to amorphous isotropic polymers, it can readily be extended to incorporate semicrystalline polymers or composites, as suitable deformation models become available.



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# *A Computer Program for Generating Deformation Mechanism Maps for Polymers*

## *1. Introduction*

The deformation mechanism map is a means of representing the predominant mechanism of deformation within a material over a range of deformation conditions. Mechanism maps have been developed to describe creep behaviour in crystalline materials such as metals and ceramics [1, 2], and more recently to describe deformation within polymers [3-5]. The program described here identifies "fields" within extension rate-temperature space where particular deformation mechanisms operate. This program delineates these mechanism fields using borders, and includes isobars to indicate stress levels.

The program utilizes both theoretical and semi-empirical models of deformation behaviour, and while in its present form it is restricted to amorphous isotropic polymers, it can be readily extended to incorporate other polymers, for example semi-crystalline, when suitable deformation models become available.

The success of a program such as this one can be measured by its ability to simulate a purely empirical map constructed from experimental test data. The deformation mechanism map generated by this program for PVC will be seen to be in very good accord with experimental data in both the prediction of deformation mechanisms and the associated stress levels. This program has been used subsequently as a basis for generating mechanism maps by Edward and co-workers [3, 5].

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## 2. Operation of the Program

Basically, the program contains a number of subroutines which comprise expressions, derived from theories describing deformation within polymers by different mechanisms, which relate the stress necessary for operation of each mechanism to the extension, rate of extension, temperature and other material properties. At each value of these parameters within the extension rate-temperature space of interest, the computer can readily calculate the mechanism which requires the least stress and indicate this on a map. A computer flow chart describing the major features of the program is shown in Figure 1.

However, since the modulus of a polymer is ordinarily dependent on both time and temperature it is necessary to first model these dependencies so that appropriate values can be used in those equations which require modulus data. This program accepts a relaxation spectrum consisting of up to 5 discrete sets of relaxation times and strengths. For the present example these relaxation times and strengths are chosen empirically to model the known time dependence of a particular modulus. The temperature dependence then follows from assuming that the relaxation times obey the Williams, Landel, Ferry (WLF) equation [6, 7].

### 2.1 Mechanisms of Deformation

A convenient temperature reference point for polymers is their glass transition temperature since different mechanisms dominate above and below this temperature. As there is far less known about the deformation of polymers than say metals, there are consequently only few theoretical models for deformation mechanisms within polymers. This program is therefore restricted to those few fundamental models which are reasonably well established, namely: viscoelasticity, rubber elasticity ( $T > T_g$ ), Argon plasticity ( $T < T_g$ ) and Newtonian viscosity ( $T > T_g$ ).

#### 2.1.1 Rubber Elasticity, $T > T_g$

A model which incorporates the strain rate dependence of rubber elastic behaviour has been developed [8, 9] through consideration of effective crosslinks (molecular entanglements) within a polymer and the thermally activated slipping of a molecule through such a restriction. The stress required to achieve an elongation,  $\lambda$ , at a constant elongation rate,  $\dot{\lambda}$ , is given by [8, 9]

$$\sigma_E = NKT \exp(Q/KT) (\dot{\lambda}/\lambda)^m$$

where  $N$ ,  $Q$  and  $m$  are material constants.

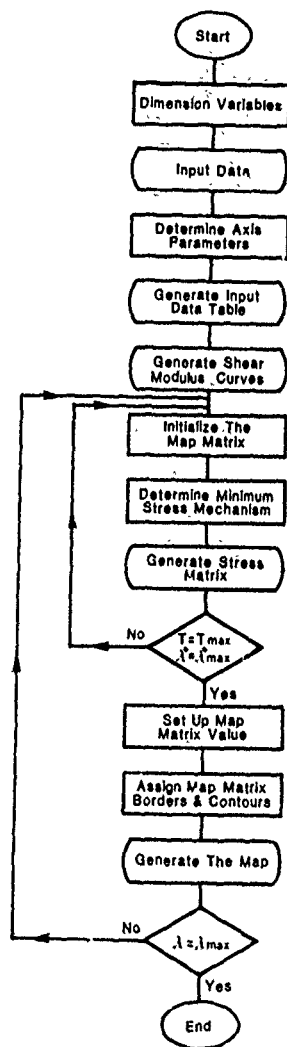


Figure 1: Computer flow chart outlining the basic operation of the program.

### 2.1.2 Viscoelasticity, All $T$

By specifying a time, and therefore temperature, dependent modulus of elasticity, a mechanism of deformation is necessarily implied. This being viscoelasticity. To calculate the stress supported by this deformation mechanism it is necessary to substitute the modulus into the Boltzmann superposition equation and evaluate this for a constant elongation rate (for small extensions).

The relevant equation is

$$\sigma_v = \dot{\lambda}/\lambda \int_0^t G(t-s) ds$$

where  $G(t)$  is determined through substitution of the relaxation spectrum.

### 2.1.3 Argon Plasticity, $T < T_g$

This mechanism, proposed by Argon [10], involves the local rotation of molecular segments towards alignment with the tensile axis. This is achieved, according to Argon, through the introduction of kink pairs along the molecule which enable it to partially "unfold" and extend further in the tensile direction. The stress required for this mechanism to operate may be represented by [10]

$$\sigma_A = c_1 G \left( 1 - c_2 kT \ln(\dot{\lambda}_0/\dot{\lambda}) \right)^{6/5}$$

### 2.1.4 Newtonian Viscosity, $T > T_g$

At sufficiently warm temperatures or long times the molecules within a polymer may to some extent disentangle themselves by sliding past one another in a process termed "reptation" [11]. This form of deformation is termed viscous flow and depends on temperature through the viscosity term  $\eta(T)$ . Van Krevelen [12] has shown that relaxation times associated with the temperature dependence of  $\eta$  obey the WLF equation for  $T_g < T < 1.2 T_g$ , and an Arrhenius activation energy law for  $T > 1.2 T_g$ . The stress can be written in terms of the extension rate as follows [12]

$$\sigma_N = \dot{\lambda}/\lambda (\eta(T)/3)$$



## **2.2 Input Data**

The program requires that a data file be created in a particular format so that material properties can be read in along with specific data according to the requirements of the individual mechanism models. When a data value is not required for the mechanism of interest, i.e. modulus relaxation times for a crystalline phase when considering an amorphous polymer, suitable values should be substituted in the input data in the appropriate format (for example, 0.0 or 1.00E+00).

### **2.2.1 General Data**

Data which are general to the mechanism models but specific to the particular polymer includes modulus data (both shear and Young's) in both the relaxed and unrelaxed state (including a spectrum of relaxation times and strengths and whether the modulus obeys an activation energy law or the WLF equation), the polymer melt and glass transition temperatures, and the percentage crystallinity for a semi-crystalline polymer.

### **2.2.2 Mechanism Specific Data**

Also required for the program is data that are essential to the calculations performed for each deformation mechanism. This information includes such data as the activation energies for specific events, separation between molecular kinks, molecular radius and molecular frequency required for Argon plasticity and the glass transition temperature viscosity for Newtonian viscosity.

Examples of input data for PMMA, PVC, PET and PC are included in Appendix 1.

## **2.3 Output Data and Maps**

The program is capable of listing all the input data in table form, graphing the variation of the moduli with both time and deformation temperature, creating a table showing the stress required by each deformation mechanism to operate at each deformation temperature, and producing the final mechanism map showing dominant mechanisms, boundaries between mechanisms and stress isobars in extension rate-temperature space. An example of computer generated moduli plots and mechanism maps for PMMA are shown in Appendix 2.

### 3. Correlation of Deformation Maps with Empirical Results

An empirical deformation map can be constructed by examining experimental data and empirically deducing which deformation mechanism is most likely operating and noting the extension, extension rate, stress and temperature values for which this occurs. Plotting this information on a map of extension rate against temperature (normalized with respect to the glass transition temperature) generates an empirical mechanism map which can be compared with that predicted by the computer program. A comparison of Figures 2 and 3 shows reasonable agreement between the empirical and theoretical maps and gives some confidence in the use of the theoretical maps to predict deformation behaviour.

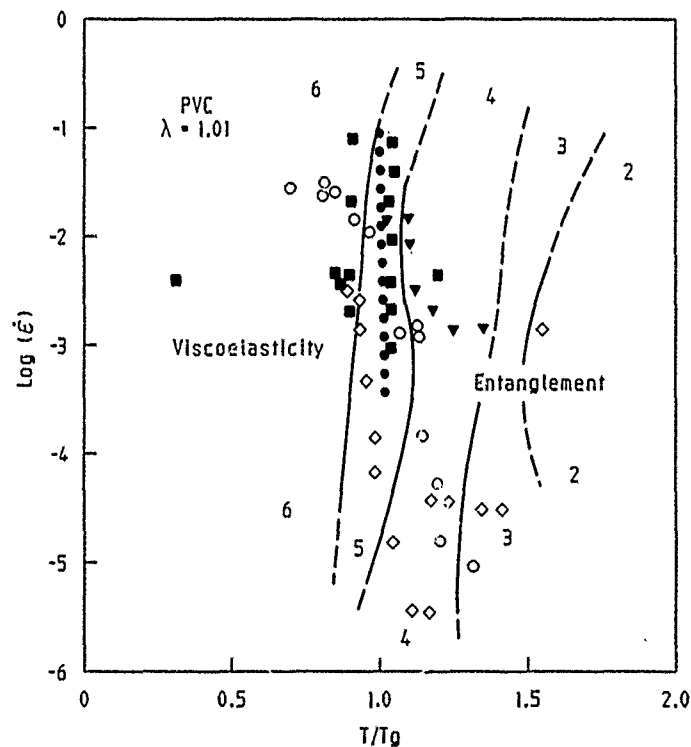


Figure 2: Empirical deformation mechanism map showing experimental data points, the logarithmic stress levels associated with these data points (e.g. 5 =  $10^5$  Pa, with solid lines representing boundaries for order of magnitude stress increases) and the border between mechanism fields (\*). Reproduced from reference [3].

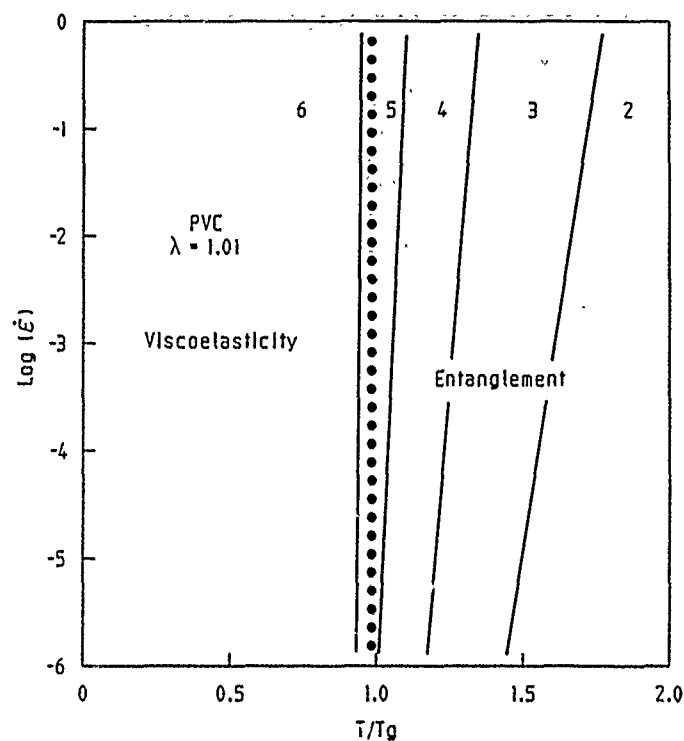


Figure 3: Theoretical deformation mechanism map showing logarithmic stress levels (e.g.  $4 = 10^4$  Pa, and solid lines represent boundaries for order of magnitude stress increases) and the border between mechanism fields (\*). Reproduced from reference [3].

#### 4. Conclusion

A program has been presented that is based on various theoretical models for polymer deformation and is able to deduce which of the mechanisms proposed by the deformation models is most likely to operate at any given combination of extension rate and temperature. The program then generates a deformation mechanism map in extension rate temperature space indicating the fields in which each mechanism dominates and the stress levels at which these mechanisms operate.

The deformation mechanism map so produced for PVC is seen to closely resemble a similar map deduced solely from experimental observations giving some confidence in the predictive capabilities of the program.

## 5. Acknowledgements

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## 7. Nomenclature

$\lambda$	elongation
$\dot{\lambda}$	elongation rate
$T$	temperature
$k$	Boltzmann's constant
$N$	number
$Q$	activation energy for entanglement slipping
$m$	strain rate sensitivity
$G$	shear modulus
$t$	time
$\eta$	viscosity
$C_1, C_2$	constants

## Appendix 1

Computer input data for a number of common polymers sourced from experiment and the quoted references. The terminology used is fully described in the computer program.

### Polymethylmethacrylate (PMMA)

SHMOD U,R, @ NLNKR		1.10E+09	5.00E+05	1.25E+21
YMOD U,R @ XLNTY		3.20E+09	1.50E+06	0.00E+01
SHMOD UC,RC & PHI		4.30E+09	1.50E+09	0.30E+00
YMOD UC,RC & PSI		9.00E+09	4.50E+09	0.20E+00
GHE1,WECRIT,KHI		5.20E+02	9.00E-02	0.50E+00
LOG(RELXN.TIMES)AMOR	-1.00	0.00	1.00	0.00
LOG(RELXN.TIMES)CRYS	0.00	0.00	0.00	-3.87
RELAXN.STRGTH(AMOR)	0.25E+00	0.50E+00	0.25E+00	0.00E+00
RELAXN.STRGTH(CRYS)	0.00E+00	0.00E+00	0.00E+00	0.60E+00
ACT.ENERGIES(AMOR)	0.00E-09	0.00E-20	0.00E-00	0.00E-00
ACT.ENERGIES(CRYS)	0.00E-00	0.00E-00	0.00E-00	1.25E-19
OBEYS Q OR WLF(AM)	1.0	1.0	1.0	1.0
OBEYS Q OR WLF(CR)	2.0	2.0	2.0	2.0
TMELT(K),TGLASS(K)TREF		4.50E+02	3.78E+02	3.93E+02
EACT1,EMM1,ENN1		5.60E-20	1.30E-01	0.00E+00
KNKSEP,MOLRAD,MOLPBN		2.85E-09	2.85E-10	1.00E+00
OMEGA,MOLFRQ,VOLDNS		5.60E+00	1.80E+11	2.00E+28
VACT1,KKSRT,KINTST		2.0E-16	6.0	1.20E-23
ETATG,ETAAC,T,GHE2		1.00E+03	5.00E-21	0.00E-00

### Plasticized Polyvinylchloride (PVC)

SHMOD U,R, @ NLNKR		1.00E+09	7.00E+05	1.25E+21
YMOD U,R @ XLNTY		3.00E+09	7.00E+05	3.00E+01
SHMOD UC,RC & PHI		3.30E+09	7.00E+07	3.00E-01
YMOD UC,RC & PSI		9.90E+09	7.00E+07	3.00E-01
GHE1,GHE2,KHI		1.00E-01	2.00E-02	5.00E-01
LOG(RELXN.TIMES)AMOR	-5.0	-2.0	-1.0	0.0
LOG(RELXN.TIMES)CRYS	-2.0	-3.0	-4.0	5.0
RELAXN.STRGTH(AMOR)	0.50E+00	0.50E+00	0.00E+00	0.00E+00
RELAXN.STRGTH(CRYS)	0.30E+00	0.20E+00	0.50E+00	0.60E+00
ACT.ENERGIES(AMOR)	1.50E-19	1.60E-20	1.00E-10	0.00E-00
ACT.ENERGIES(CRYS)	1.00E-01	3.10E-18	3.20E-19	1.25E-19
OBEYS Q OR WLF(AM)	1.0	1.0	1.0	1.0
OBEYS Q OR WLF(CR)	2.0	1.0	1.0	2.0
TMELT(K),TGLASS(K)TREF		5.00E+02	2.70E+02	3.00E+02
EACT1,EMM1,ENN1		5.60E-20	1.30E-01	0.00E+00
KNKSEP,MOLRAD,MOLPBN		2.85E-09	2.85E-10	1.00E+00
OMEGA,MOLFRQ,VOLDNS		5.60E+00	1.80E+11	2.00E+28
VACT1,KKSRT,KINTST		2.00E-16	6.00E+00	1.20E-23

# Polyethylene terephthalate (PET)

SHMOD U,R, @ NLNKS	1.10E+09	7.00E+05	1.25E+21
YMOD U,R @ XLNTY	3.00E+09	7.00E+05	3.00E+01
LOG(RELXN.TIMES)AMOR	-3.0	-2.0	-1.0
LOG(RELXN.TIMES)CRYS	2.0	3.0	4.0
RELAXN.STRGTH(AMOR)	0.50E+00	0.50E+00	0.00E+00
RELAXN.STRGTH(CRYS)	0.00E+00	0.00E+00	0.00E+00
ACT.ENERGIES(AMOR)	1.50E-19	1.60E-20	1.00E-10
ACT.ENERGIES(CRYS)	1.00E-01	3.10E-18	3.20E-19
OBEYS Q OR WLF(AM)	1.0	1.0	1.0
OBEYS Q OR WLF(CR)	2.0	1.0	1.0
TMELT(K),TGLASS(K)FREQ	5.45E+02	3.45E+02	1.00E+00
EACT1,EMM1,ENNI	5.60E-20	1.30E-01	0.00E+00
KNKSEP,MOLRAD,MOLPBN	2.85E-09	2.85E-10	1.00E+00
OMEGA,MOLFRQ,VOLDNS	5.60E+00	1.80E+11	2.00E+28
VACT1,KKSRT,KINTST	2.00E-16	6.0	1.20E-23

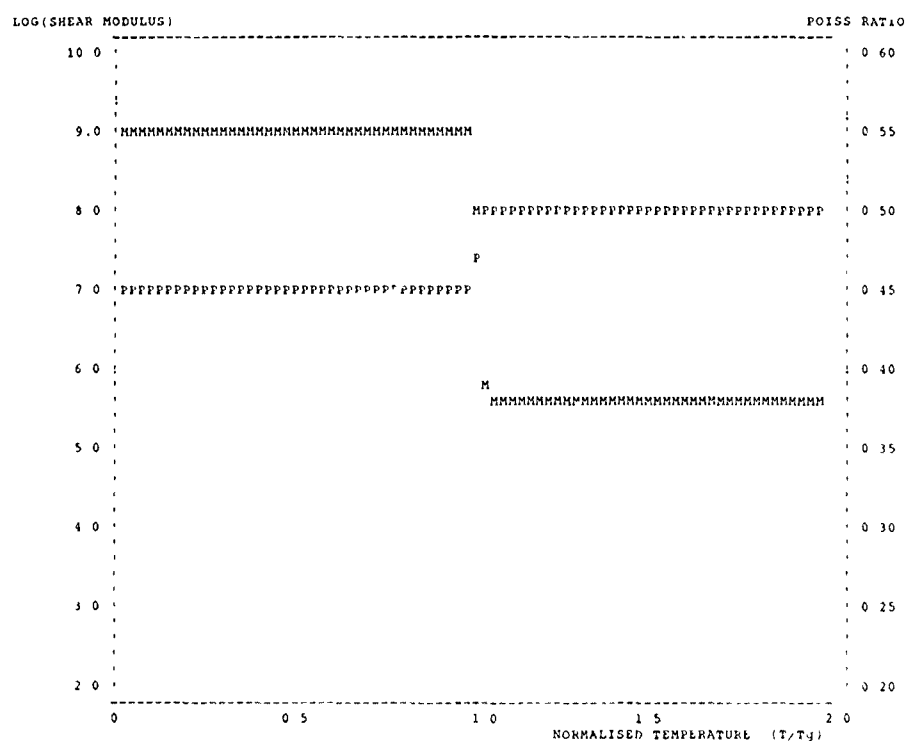
# Polycarbonate (PC)

SHMOD U,R, @ NLNKS	1.10E+09	7.00E+05	1.25E+21
YMOD U,R @ XLNTY	3.12E+09	7.00E+05	3.00E+01
LOG(RELXN.TIMES)AMOR	-3.0	-2.0	-1.0
LOG(RELXN.TIMES)CRYS	2.0	3.0	4.0
RELAXN.STRGTH(AMOR)	0.50E+00	0.50E+00	0.00E+00
RELAXN.STRGTH(CRYS)	0.00E+00	0.00E+00	0.00E+00
ACT.ENERGIES(AMOR)	1.50E-19	1.60E-20	1.00E-10
ACT.ENERGIES(CRYS)	1.00E-01	3.10E-18	3.20E-19
OBEYS Q OR WLF(AM)	1.0	1.0	1.0
OBEYS Q OR WLF(CR)	2.0	1.0	1.0
TMELT(K),TGLASS(K)FREQ	5.00E+02	3.00E+02	1.00E+00
EACT1,EMM1,ENNI	5.60E-20	1.30E-01	0.00E+00
KNKSEP,MOLRAD,MOLPBN	2.85E-09	2.85E-10	1.00E+00
OMEGA,MOLFRQ,VOLDNS	5.60E+00	1.80E+11	2.00E+28
VACT1,KKSRT,KINTST	2.00E-16	6.0	1.20E-23

## Appendix 2

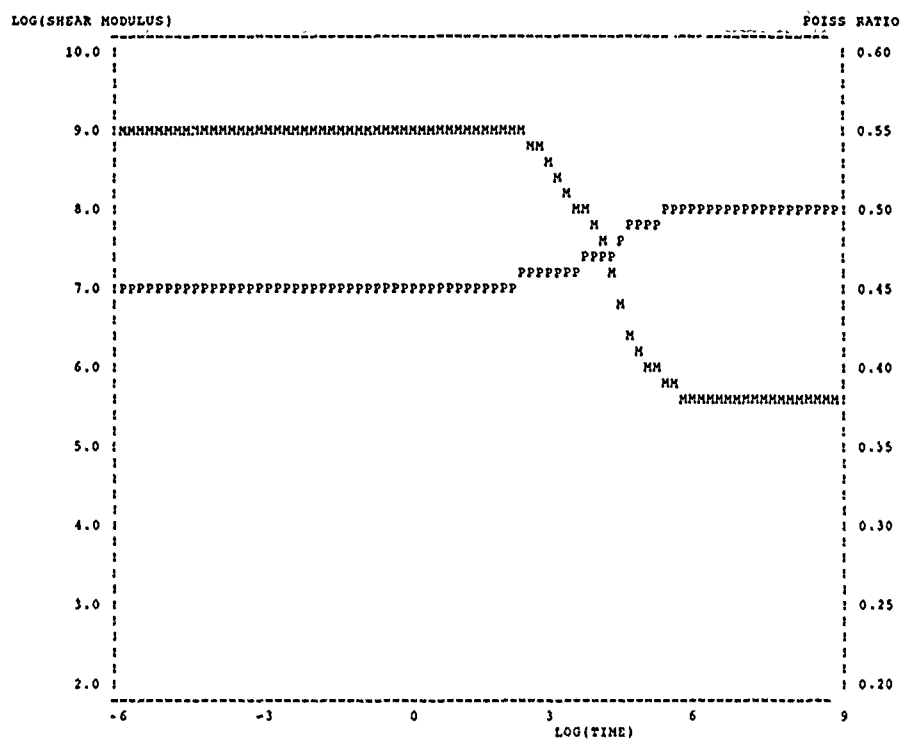
Computer generated plots of shear modulus ( $G$ ) and Poissons ratio ( $P$ ) versus (i) normalized temperature ( $T/T_g$ ) and (ii) time; and computer generated mechanism maps showing the operation of viscoelasticity ( $V$ ), rubber elasticity ( $E$ ), Argon plasticity ( $A$ ) and Newtonian viscosity ( $N$ ) within PMMA over extension rate - temperature for increasing values of extension ( $\lambda$ ). Asterisks (\*) represent borders between mechanisms and crosses (X) interspersed with numerals represent order of magnitude increases in stress magnitude, i.e.  $3 = 10^3$  Pa.

(i)

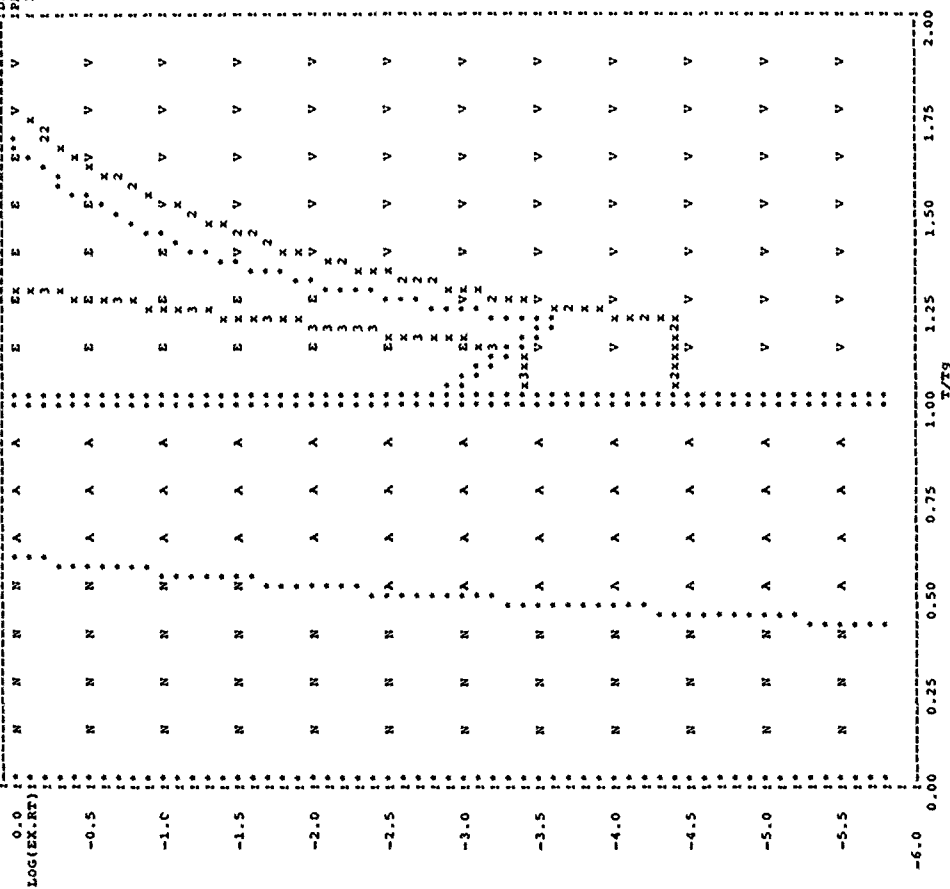




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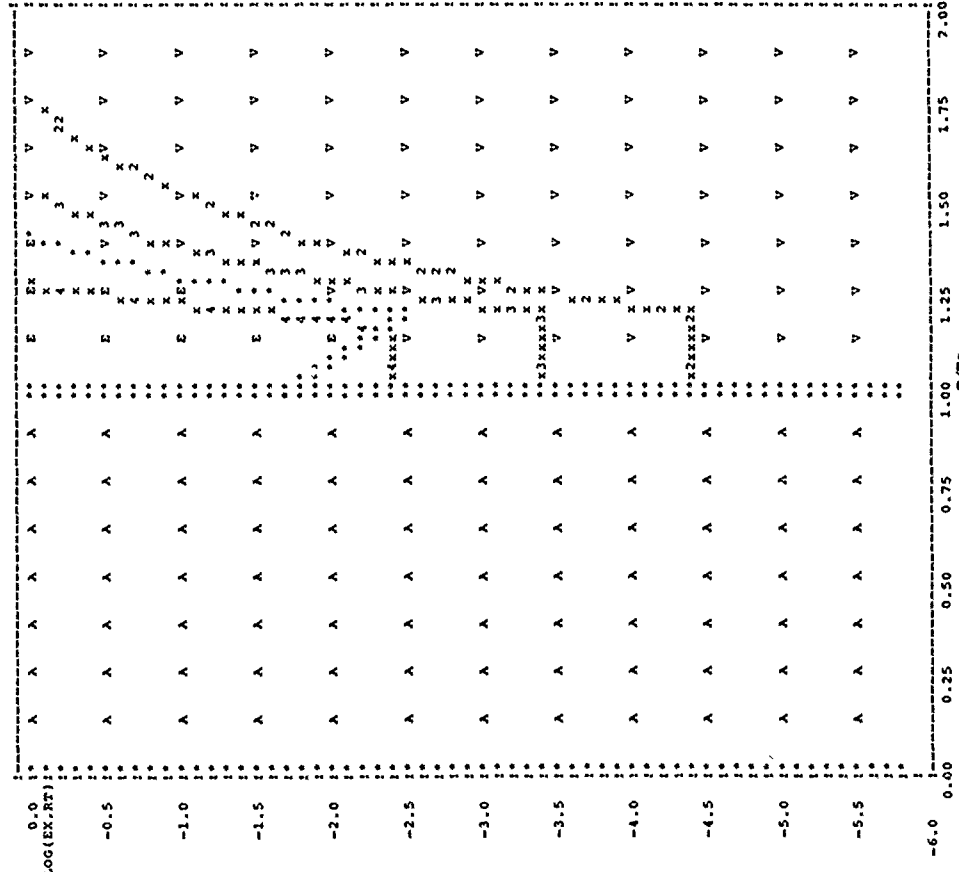


DEFORMATION MECHANISM MAP  
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 LAMBDA = 1.01

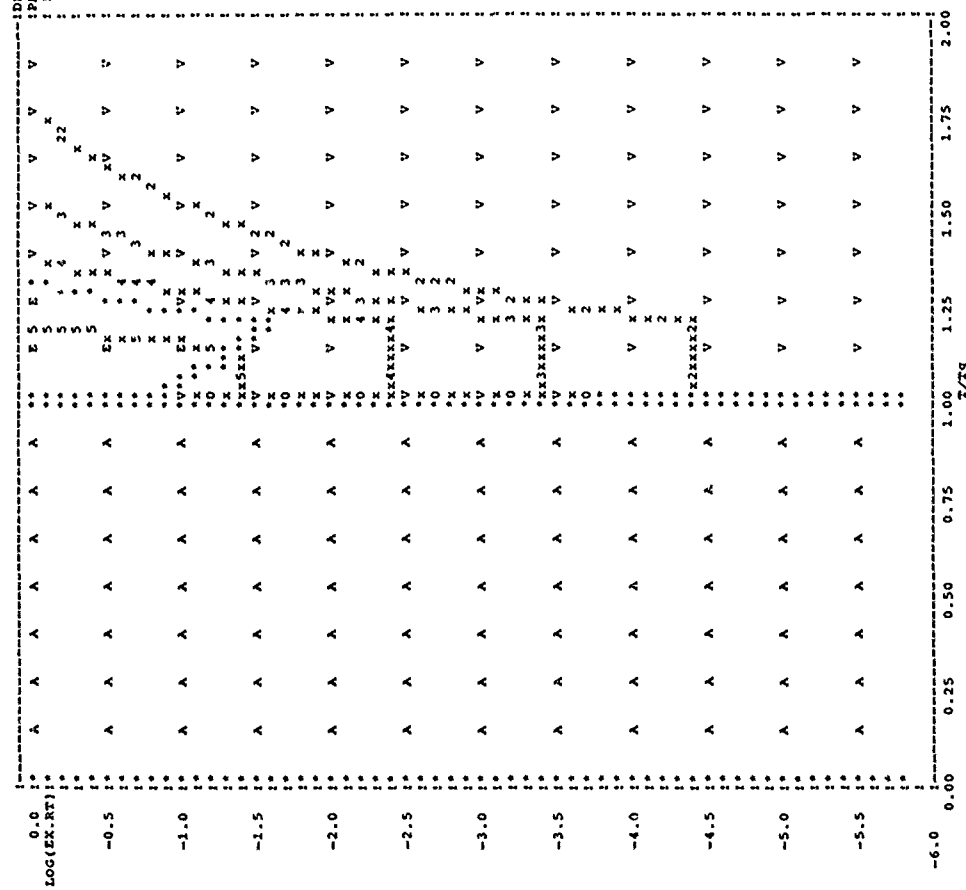


INFORMATION MECHANISM MAP

IPMAA  
LAMBDA = 1.10



DEFORMATION MECHANISM MAP  
 : PHNA  
 : LAMBDA = 2.00



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Modelling  
Rubber elasticityViscosity  
Polymer deformation

Strain rate dependence

## ABSTRACT

The deformation mechanism map is a means of representing the predominant mechanism of deformation within a material over a range of deformation conditions. This paper introduces a computer program which utilizes a number of theoretical models of deformation within amorphous polymers to identify "fields" within extension rate-temperature space where particular deformation mechanisms operate. The program is able to delineate these fields using borders and include isobars to indicate stress levels. Very good correlation is seen between the computer generated mechanism map and experimental results for PVC.

Whilst in its present form the program is restricted to amorphous isotropic polymers, it can readily be extended to incorporate semicrystalline polymers or composites, as suitable deformation models become available.

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